

Ambient Air Non-Methane Hydrocarbon Monitor

Ford Aerospace and Communications Corp.
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ABSTRACT

A monitor has been developed with adequate sensitivity and accuracy to measure continuously the concentration of non-methane hydrocarbons (NMHC) in ambient air. The monitor consists of pump and manifold system along with two basic instruments, a methane monitor and a flame-ionization detector (FID). The methane monitor, which employs gas-filter correlation techniques, makes use of the infrared absorption characteristics of methane to measure its concentration. A slight interference in the measurement of methane by H_2O vapor in the sample air is accounted for from the simultaneous measurement of the H_2O concentration. The flame-ionization detector measures the concentration of the total hydrocarbons (THC), including methane. The concentration of non-methane hydrocarbons is found by subtracting the methane concentration from the THC concentration. The noise-equivalent concentrations (peak-to-peak) of the methane monitor and the FID are approximately 50 ppb and 5 ppb of carbon, respectively. The estimated uncertainty in the measurement of a typical low-level NMHC concentration is between 20 ppb and 50 ppb. Concentrations as high as approximately 70 ppm can be measured.

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ABBREVIATIONS

AGC	-- automatic gain control
CH ₄	-- methane
FID	-- flame-ionization detector
H ₂ O	-- water
Hz	-- hertz
NMHC	-- non-methane hydrocarbons
ppb	-- parts per billion (of carbon atoms)
ppm	-- parts per million (of carbon atoms)
THC	-- total hydrocarbon
V _a	-- voltage at modulator frequency, 30Hz
V _c	-- voltage at carrier frequency, 360 Hz
V _i	-- V _a /V _c

SECTION 1

INTRODUCTION AND SUMMARY

Hydrocarbons in the atmosphere play an important role in the production of photochemical smog and are of great interest to atmospheric chemists and to those concerned with air quality. Methane, the most abundant atmospheric hydrocarbon, is essentially non-reactive at the normal ambient concentrations of a few ppm; thus this gas does not contribute significantly to atmospheric photochemistry. It follows that the quantity of most interest is the concentration of the other hydrocarbons, commonly called non-methane hydrocarbons (NMHC). For some detailed studies, it may be desirable to know the concentration of certain hydrocarbon species, but for many purposes it is sufficient to know the sum of the concentrations of all the NMHC's.

No convenient and reliable method has yet been developed for routine monitoring of NMHC's. One widely used instrument, the flame-ionization detector (FID), is capable of measuring the concentration of all the hydrocarbons, frequently called total hydrocarbons (THC). However, this quantity is not the one of most interest because it includes the inert methane, which may constitute from 30 to 90% of the THC. The present program involves coupling a commercially available FID to measure the THC concentration with a custom-designed methane monitor. The NMHC concentration is equal to the difference between the concentrations measured by the two instruments. The methane monitor uses gas-filter correlation techniques and contains a set of multiple-pass optics to give an 845 cm absorption path. Water vapor in the air sample interferes with the methane measurement, giving a false reading that depends on the partial pressure of the H_2O vapor. An infrared H_2O monitor built as an integral part of the methane monitor measures the H_2O concentration, making it possible to account for the interference. A diaphragm pump circulates either sample air, bottled zero-gas or bottled span gas through the monitors. The span calibrations of both the methane monitor and the FID are quite stable. Slight drifts in the zero settings of both instruments make it necessary to flush the sample chambers with zero-gas approximately once each hour if the most accurate results are required. The estimated uncertainty in a measurement of a typical NMHC concentration below 1 ppm (parts per million of carbon) is between 20 and 50 ppb (parts per billion of carbon).

SECTION 2

CONCLUSIONS

It has been demonstrated that an instrument consisting of a methane monitor combined with a FID can be designed and built with adequate sensitivity and accuracy to monitor ambient NMHC concentrations under most conditions of interest. The low concentrations of hydrocarbons make it necessary that both of the instruments be very sensitive and stable. It is desirable that the instruments be kept in a temperature controlled room and the sample air be drawn in from the outside through a heated line. Care must be exercised to avoid contaminating air samples and calibration gases or losing hydrocarbons on the walls of the gas handling system. Activated charcoal filters in the fuel line and combustion-air line of the FID remove any residual hydrocarbons in these gases and lead to greatly improved instrument stability. A single pump of the proper design can circulate the air sample through both the methane monitor and the FID. No changes in the hydrocarbon concentration of an air sample appear to take place when it passes through a diaphragm pump with the interior teflon coated and properly cleaned copper tubing heated to approximately 50 °C.

A standard sensor (combustion chamber plus electronics) for a FID provides adequate sensitivity when operated with a convenient fuel mixture of 40% H₂ + 60% He. The short-term peak-to-peak noise (period less than 10 sec) can be made less than the equivalent of 5 ppb of methane for the FID and less than 50 ppb of methane for the methane monitor. Longer-term drift of the zero-settings of the instruments normally leads to uncertainties in the measurements that are somewhat larger than those imposed by noise unless the drift is accounted for by flushing the sample chambers once every few minutes with zero-gas. Stability of the methane monitor is improved greatly by controlling the temperatures of the sample cell, bandpass filter, and gas-filter cell of the methane monitor.

Interference by H₂O in the air limits the accuracy of the methane monitor unless most of this gas is removed from the air before it enters the methane sample cell. One acceptable method of accomplishing this is to pump the air through a Perma-Pure Dryer before it enters the methane sample cell. Air going to the FID should by-pass the dryer to avoid possible adsorption of some of the complex hydrocarbons on the walls of the dryer. The H₂O interference can also be accounted for by measuring the H₂O concentration in the methane sample cell and applying a correction based on interference data obtained previously with samples of H₂O plus clean air.

SECTION 3

RECOMMENDATIONS

Additional tests should be carried out with the instrument under a variety of laboratory and field conditions to gain more information about the detailed performance. After these tests have been completed, a prototype instrument should be designed and built to operate on the same basic principles as the present instrument. This instrument should include a FID to measure THC concentrations and a methane monitor that employs gas-filter correlation techniques.

The following features and procedures are recommended for the prototype instrument. Many of these features are included in the present instrument and have proven to be desirable; others are recommended as a result of knowledge gained while assembling and testing the present instrument. Important features of the present instrument that are not mentioned below should be included.

Package both the FID and methane monitor into a single unit.

Use the combustion chamber from a commercially available FID with combustion fuel of 40% H_2 and 60% H_e .

Pump sample air through heated lines to both the methane monitor and the FID with a single diaphragm pump capable of producing pressures up to 5 atm. Split the gas flow so that the gas to the FID does not pass through the methane sample cell. Include in the line to the FID a small "delay tank" so that at a given time the FID is sampling air that entered the inlet line over the same period of time as the air in the methane sample cell.

Pass the air to the methane sample cell through a dryer such as a Perma-Pure Dryer to remove most of the H_2O vapor and thus reduce the interference by this gas in the measurement of methane concentration.

Employ activated charcoal filters, or some substitute, in the lines for the combustion-air and fuel.

Operate the sample cell of the methane monitor between 3 atm and 5 atm to increase sensitivity and reduce interference due to residual H_2O . This also improves the efficiency of a dryer similar to the Perma-Pure Dryer.

Decrease the volume of the methane sample cell and use multiple-pass optics in the cell to obtain a sample path length between approximately 8m and 15m. Shape the sample cell to reduce the volume while passing approximately the same amount of radiation in the monitoring beam as the present instrument.

Control the temperatures of: (a) methane gas-filter cell, (b) spectral bandpass filter for methane monitor, (c) methane sample cell, and (d) regulators, valves, tubing etc., that are parts of the FID. Heat gas lines, including the dryer, to approximately 50°C; it is not necessary to control the temperature of these lines.

Include electronics to measure directly the difference between the output signals of the FID and methane monitor; this voltage is proportional to the NMHC concentration.

SECTION 4

GAS HANDLING AND SAMPLING

Figure 1 shows a diagram of the gas-handling system for the methane monitor and FID coupled together. When these two monitors are connected as shown it is possible to measure simultaneously the concentrations of methane and THC in air. The output signal of the FID is nearly proportional to the number of carbon atoms in all of the hydrocarbons, including methane. The difference between the two values measured is therefore approximately proportional to the concentration of carbon atoms in the non-methane hydrocarbons (NMHC), the quantity of primary interest. Slight differences in the sensitivity of the FID to different hydrocarbons are discussed in Section 7.

The optimum pressure in the sample chamber of the FID is slightly above 1 atmosphere, whereas the methane sample cell can operate at any desired pressure from less than 1 atm to more than 2 atm. The optimum sensitivity would occur between 2 atm and 5 atm; however, the pump and methane sample cell in the present instrument are not designed for efficient use above approximately 2 atm. We recommend operating at 2 atm, although lower pressures may be used if the sensitivity is calibrated for the pressure used.

The volume of the methane sample cell is approximately 2 liters; at typical sample flow rates, between 20 seconds and 2 minutes are required to displace all of the gas in the cell. Thus, if there is a sudden change in the concentration of methane in the air being sampled, the monitor indicates a gradually changing concentration while the gas in the sample cell changes. It is important that the FID sample air at any given time consists of approximately the same ratios of "old" and "new" air as are in the methane sample cell. This is essentially accomplished by extracting gas for the FID from the methane sample cell through several small holes distributed along the length of the cell. Because of the small volume of the line from the methane sample cell to the FID, there is only a few seconds delay from the time a volume of gas is in the methane sample cell until it reaches the sampling chamber of the FID.

Most of the gas entering the methane sample cell exits to the atmosphere through the back-pressure regulator which is adjusted to maintain the desired pressure in the methane sample cell. Adjustable valves on the FID determine the flow-rate to the FID. The total flow to the methane sample cell is determined by valves in the line ahead of the sample cell. A pressure-control switch connected to the line near the pump discharge automatically shuts off the power to the pump if the pressure gets high enough that it might damage the pump.

A two-way solenoid valve directs gas to the pump from either the air inlet or bottled gas. The solenoid valve can be switched from one position to the other by a manually operated electrical switch or it can be connected to a timer. During normal

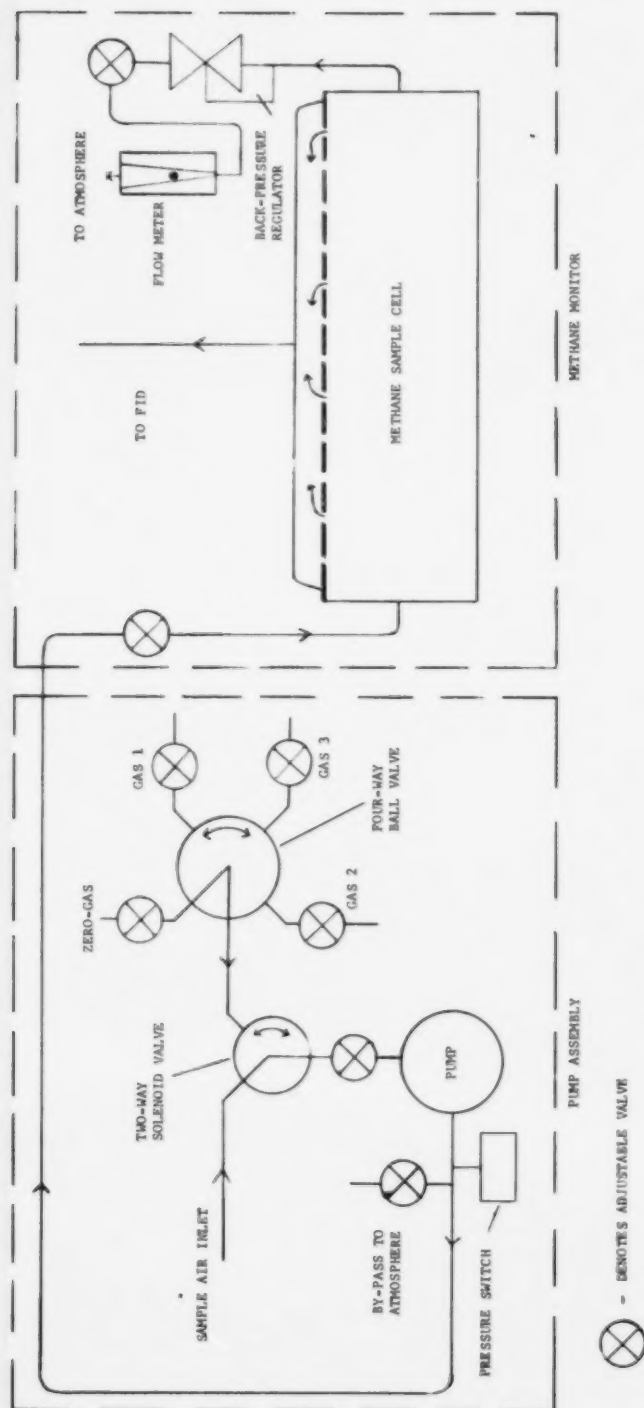


Figure 1. Schematic diagram of the gas-handling system.

monitoring, ambient air is sampled continuously for a period of approximately one or two hours, then the solenoid valve is switched to accept zero-gas for a few minutes. The valve then switches back to the ambient air sample. This procedure makes it possible to account for drift in the zero-settings of the two monitors. The span calibration of the methane monitor is quite stable and needs to be checked only once each few days. The span calibration of the FID is also quite stable if the flow-rate through the sampling chamber is maintained constant.

As many as four bottles of zero-gas or span gas can be connected simultaneously to the gas-handling system. The bottle from which gas is withdrawn at any time is determined by the position of a four-way ball valve. Valves on the lines connecting the gas bottles to the four-way ball-valve are adjusted so that the flow rate is approximately the same as the flow-rate of ambient air.

The methane sample cell is temperature-controlled at approximately 50°C to help maintain stability of the optics and to avoid condensation of H₂O. Electrical heaters are also attached to the inlet line for ambient air and to all of the lines through which gas passes after it leaves the pump.

SECTION 5

METHANE MONITOR

LAYOUT AND OPTICAL DIAGRAM

Figure 2 shows the layout and the optical components of the methane monitor. Radiant energy from the source, a tungsten-iodide bulb, enters the heated enclosure that surrounds the gas-filter cell (GFC) assembly. Lens L1, which serves as an entrance window, forms an image of the source on the slit (slit 1) mounted on the inside wall of the heated enclosure. Flat mirror N1 rotates the converging beam from lens L1 by 90° so that it passes through the rotating GFC assembly approximately 2 cm below the axis of rotation. A reticle attached to the rotating GFC assembly chops the beam at 360 Hz. Field lens L2 serves as an exit window for the heated enclosure and forms an image of lens L1 near mirror N3. Mirror N3, with a focal length of 7.5 cm, forms a magnified image of slit 1 next to the front surface of mirror C2 in the sample cell. Lens L3 functions both as an entrance window for the sample cell and as a field lens that images mirror N3 near mirror C1.

The multiple-pass sample cell, described in more detail below (under "Sample Cell"), is adjusted to operate at 20 passes, giving an optical path length of 845 cm. The beam emerging from the sample cell passes through quartz lens L4, which nearly collimates the beam before it passes through the narrow-bandpass filter. Detector lens LD images slit L1 on the detector, which has a 2 mm x 2 mm sensitive element that is thermoelectrically cooled to approximately -20°C. The filter passes a narrow spectral band near 3.3 μ m that contains strong absorption lines of methane. The filter is mounted in a small sub-assembly that is temperature controlled at approximately 50°C to maintain the center of the spectral bandpass at a carefully determined wavelength. The stable spectral bandpass is required for a stable zero-setting.

SAMPLE CELL

The sample cell body consists of a 45-cm long piece of 7.6-cm ID (3.0") stainless steel tubing with flanges welded to each end. The flanges provide support for the various mounts and adjustment plates for the multiple-pass optics. End covers are screwed to each flange and O-rings provide leak-proof seals. Optical path lengths of 195 cm to 1332 cm may be obtained by adjusting the multiple-pass optics; it is intended that the optics remain adjusted to 20 passes.

The cell is maintained at 50°C by a temperature controller that controls the average power dissipated by the heaters. One heater is coiled around the cell body, and a power resistor mounted on each end plate provides additional heat at the ends. The endplates are within $\pm 2^\circ\text{C}$ of the cell body when the cell temperature is stabilized. The temperature near the center of the cell body may be determined by monitoring the output of an iron-constantan thermocouple embedded in the cell body. Foam-rubber

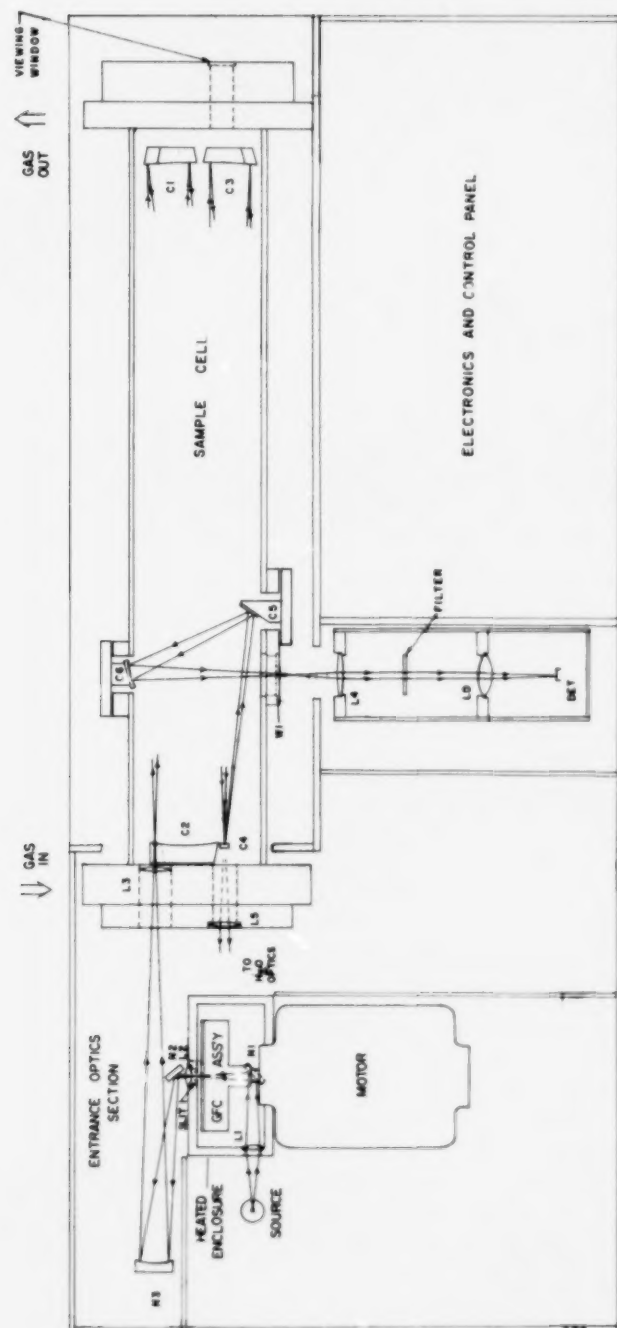


Figure 2. Layout and optical diagram of the methane monitor.

insulation is wrapped around the cell body and secured with aluminum tape; black foam rubber insulates the ends. The cell is welded to two stainless steel mounting plates, which are spaced off the base plate with 1.27 cm (0.5") thick phenolic spacers to minimize conductive heat losses through the baseplate.

Gas flows into and out of the cell through tubing attached to the 1/4" Swagelok fittings. Gas enters the end of the cell to which mirror C2 is attached and exits the cell at the opposite end, as indicated in Figure 2.

Figure 2 illustrates the multiple-pass optical components mounted inside the sample cell. Spherical mirrors C1 and C3 are cut from the same mirror blank with a radius of curvature of 40.6 cm (16"), the distance between the front surfaces of mirrors C1 and C3 and the front surface of spherical mirror C2. The radius of curvature of mirror C2 is also 40.6 cm. The magnified image of slit 1 formed by mirror N3 is adjacent to the front surface of C2. Mirrors C1 and C3 form multiple images of slit 1 on mirror C2. The number of images, and thus the number of cell passes made by the beam, can be set by adjusting the azimuth adjustment screw for mirror C2. Figure 3 illustrates the image pattern on mirror C2 as seen through the viewing window when the cell is adjusted for 20 passes.

Part of the beam from mirror N3 spills over mirror C1 onto mirror C3, which forms an image of slit 1 adjacent to mirror C2 near lens L5. This beam of energy exits the sample cell after only 2 passes and is used in the H₂O correction system discussed in Section 6. After passing through the sample cell 20 times, the main beam is incident on mirror C4 (focal length = 15.0 cm). This mirror is adjusted to make the beam strike flat mirror C5, which directs the beam to spherical mirror C6. Mirror C6, with a focal length of 6.0 cm, forms an image of slit 1 near the anti-reflection coated sapphire window at the exit port of the sample cell.

GAS-FILTER CELL AND PRINCIPLES OF DETECTION

Much of the good stability and high sensitivity of the instrument is due to the rotating gas-filter cell, which is illustrated in Figure 4. Compartment GC1 is filled with 0.6 atm of a 25% CH₄ + 75% N₂ mixture to form the gas filter. Compartment GC2 is filled with 0.5 atm of non-absorbing N₂. The 5.1 cm (2 inch) diameter sapphire windows are anti-reflection coated with a single dielectric layer to provide high transmittance near 3.3 μ m. Enough of the methane mixture is introduced in the compartment GC1 so that its average transmittance, combined with the windows, is the same as the average transmittance of the windows with the attenuator in compartment GC2. The cell body is made of stainless steel, and it can be refilled through a small port on the outer edge of the cell. The optical path through the methane in compartment GC1 is approximately 1 cm.

A reticle deposited on the surface of one of the rotating cell windows has 12 opaque strips and 12 openings to produce a high-frequency chopping rate of 360 Hz. When methane is added to the sample section, it absorbs a fraction of the chopped energy that passes through the attenuator side of the rotating cell. However, when the gas-filter side, GC1, of the rotating cell is in the beam, the gas-filter cell absorbs most of the energy at wavelengths where the methane in the sample cell

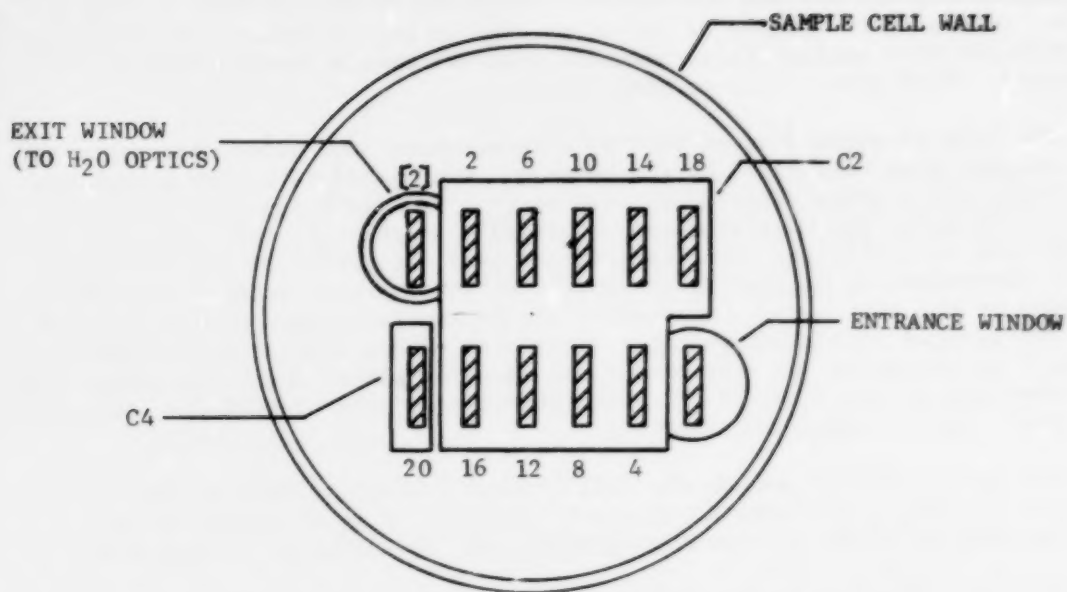


Figure 3. Images formed by multiple-pass cell optics on mirror C2. Numbers by the images indicate the number of passes of the beam through the sample volume when the image is formed.

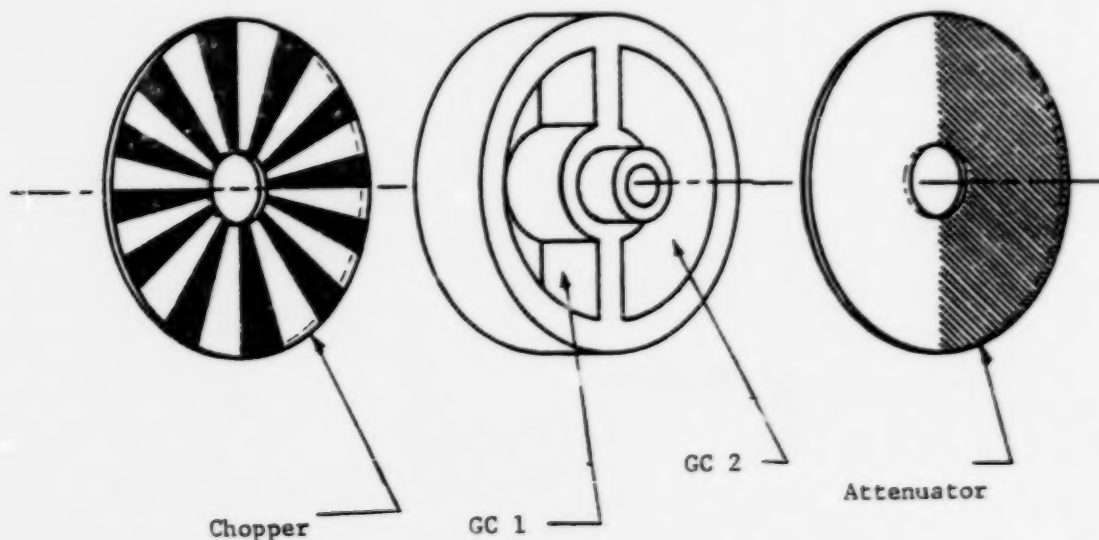


Figure 4. Exploded view of the rotating gas-filter cell.

absorbs. Therefore, the addition of methane in the sample section decreases the energy passing through GC2 more than it reduces the energy through GC1. Thus, the 360-Hz chopped signal contains a modulation at 30 Hz, the rotational frequency of the gas-filter cell. The amount of modulation depends on the product of the methane concentration in the sample cell and the pathlength in the sample section. The detector signal is processed by the electronics to produce a dc output signal proportional to the fractional modulation of the energy incident on the detector, and thus to the concentration of methane in the sample cell.

Any absorbing gas species other than methane in the sample cell will not produce a 30-Hz modulation if there is no correlation between the spectral structure of the gas and the spectral structure of the methane in the gas-filter cell. When there is no correlation between the spectral structures, the gas absorbs exactly the same fraction of the energy passing through the gas-filter cell as that passing through the attenuator. Thus, under this idealized condition, no 30-Hz modulation is produced and there is no interference in the output signal by the gas. Of course, the instrument can not operate properly if the absorbing gas absorbs a large fraction of the radiant energy incident on it. Unfortunately, there is usually a small amount of correlation between the spectral structures of the gas species to be detected and another gas that absorbs in the same spectral region. The most serious interfering gas for the present instrument is H_2O . There is a slight positive correlation between the spectral structures of methane and H_2O in the spectral bandpass of the instrument. Thus, the H_2O produces a positive interference signal. A few other gases, including butane and propane, interfere slightly, but the concentrations of these gases are normally so low in ambient air that the interference is negligible.

ELECTRONICS AND PROCESSING OF DETECTOR SIGNAL

The electronics process the signal from the detector and produce a dc voltage that is proportional to the concentration of methane in the sample gas. The relationship between the output voltage and the methane concentration is determined by calibrating the instrument with samples of known concentration. A block diagram of the electronics used to process the photodetector signal is shown in Figure 5. The 360-Hz component of the signal from the detector serves as the carrier for the 30-Hz component that is to be measured. The 30-Hz component of the detector signal resulting from any 30-Hz variation of radiant energy on the detector that is not also chopped at the carrier frequency is rejected by the electronics. The electronics consist basically of two demodulators in series. The first demodulator operates at the carrier frequency, 360 Hz; the average output of this demodulator is proportional to the amount of radiant energy chopped at 360 Hz. If the chopped energy incident on the detector is also modulated at 30 Hz, the 30-Hz component of the output signal from the 360-Hz demodulator is proportional to the modulation. This 30-Hz component then passes through a series of gain controls and amplifiers to the 30-Hz synchronous demodulator. The output of the 30-Hz synchronous demodulator is proportional to the 30-Hz modulation of the 360-Hz signal, and thus to the concentration of methane in the sample gas. The reference signal for the 30-Hz synchronous demodulator is supplied by the 30-Hz reference pick-up mounted on the heated enclosure.

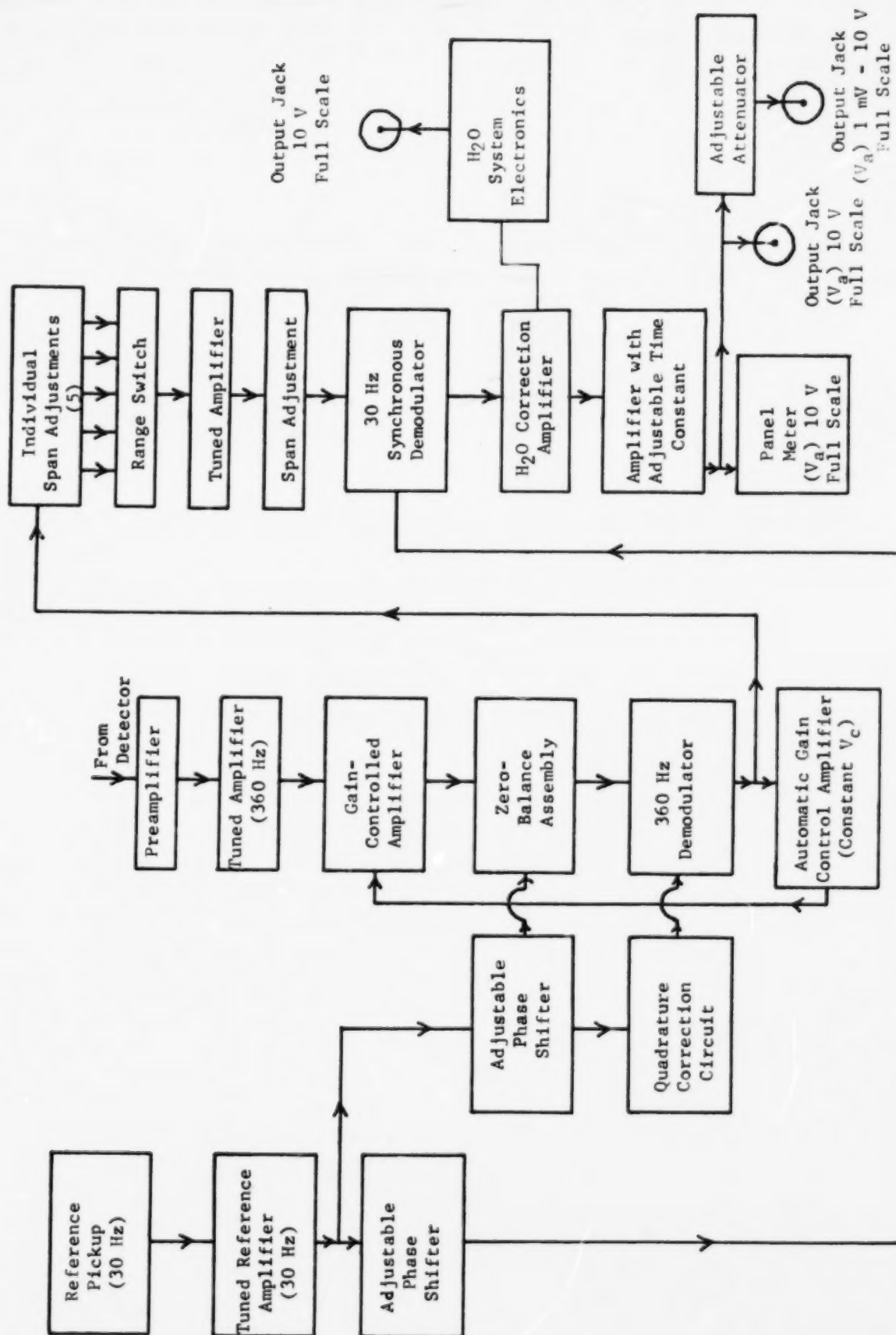


Figure 5. Block diagram of the signal-processing electronics.

When H_2O is in the sample gas, the 30-Hz signal also contains a component due to the H_2O . This interference is partially accounted for electronically by an H_2O monitor described in Section 6. The H_2O monitor produces a dc signal that is approximately proportional to the concentration of H_2O in the sample cell. This signal is fed into the " H_2O Correction" circuitry as illustrated in Figure 5 to apply a correction signal in the main electronics that process the signal from the detector in the methane channel. In several instruments built previously, we have been able to correct automatically for H_2O interference in this way. As discussed below in Section 6, the interference is only partially accounted for in this instrument. However, the amount of additional correction that is required can be determined from the measurement of the H_2O concentration.

A time constant switch mounted on the main electronics card makes it possible to select an electronic time constant of 0.3, 1, 3 or 10 sec. The main output signal can be determined from a panel meter or from either of two output jacks. A signal that corresponds to a full-scale reading of the panel meter produces a 10-volt dc signal on one of the output jacks. The corresponding full scale reading for the other output jack can be adjusted from less than 1 mv to 10 v. Thus, the instrument can be used with a wide range of recorders or meters, provided the input impedance of the recorder is sufficiently high.

During the normal mode of operation it is desirable that the output signal be proportional to the ratio, $V_a/V_c = V'$, where V_a is the average demodulated 30-Hz component of the detector signal and V_c is the 360-Hz component of the detector signal. The instrument calibration relates the methane concentration of the sample gas to V' , and it is desired that this relationship be independent of source brightness, detector sensitivity, etc. During the normal mode of operation, V_c is maintained at a constant value by the automatic gain control (AGC) circuits. If, for example, the signal from the photodetector decreases because of dirt on a window or a decrease in source brightness, the AGC increases the amplification of both the 360-Hz signal and the 30-Hz signal by the same factor. Therefore, V' is kept directly proportional to the output V_a and maintains a constant relationship with the methane concentration.

A four-position switch mounted on the main electronics card makes it possible to use the panel meter to monitor quantities other than the signal output. The 30-Hz reference signal and the average carrier voltage, V_c , can be checked with this meter to see if they are in the correct operating range. When the selector switch is in the "signal-in" position, the meter reads the level of the signal going into the 360-Hz synchronous demodulator. With the selector switch in the "signal out" position, the meter reads the level of the output signal. The signals on the output jacks are not affected by the position of the selector switch.

The modulation signal on the carrier may have a quadrature component that is 90° out of phase with the reference signal and results from irregularities in the gas-filter cell assembly generated during fabrication. A quadrature correction circuit is adjusted during alignment to cancel electronically the quadrature component of the 30-Hz modulation. No quadrature correction is required for this instrument; therefore the gain of the correction circuit has been turned to zero.

The 30-Hz reference pickup consists of a light-emitting diode (LED) and a small phototransistor. The 30-Hz pickup is mounted on the heated enclosure for the GFC assembly. Aluminum tape is wrapped around half the circumference of the reticle, and the other half is black. As the GFC assembly spins at 1800 rpm, light from the LED is reflected by the aluminum tape but not by the black area. The reflected light is sensed by the detector and produces a 30-Hz signal. The amplifier for the 30-Hz reference pickup is tuned and contains an adjustable phase shifter to produce a "clean" signal with the proper phase for the 30-Hz synchronous demodulator.

The zero-balance assembly electronically accounts for any misbalance between the two halves of the gas-filter cell assembly cycle when there is no methane in the sample cell. This electronics assembly would not be required if it were practical to maintain a perfect optical balance between the two halves. Approximately ± 10 percent variation in the transmittance through either of the two halves of the cycle can be accounted for by this electronic zero-balance assembly. The assembly changes the amplification ahead of the 360-Hz demodulator during the two halves of the GFC assembly cycle. A signal from the 30-Hz reference pickup switches the zero-balance assembly between the two different gains with the proper phase. The difference in the gains between the two halves is adjusted with the "zero" potentiometer mounted on the top of the instrument.

SECTION 6

H₂O MONITOR

The H₂O monitor is built as an integral part of the methane monitor with several of the optical components shared by both the H₂O and methane channels. The H₂O monitor produces a dc voltage that is nearly proportional to the concentration of H₂O in the multiple-pass sample cell. The interference on the methane channel by H₂O is also approximately proportional to the H₂O concentration. An output signal from the H₂O monitor is fed into the methane channel as illustrated above in Figure 5 to correct automatically for the H₂O interference. Unfortunately, it is not possible to correct automatically for the H₂O interference with adequate accuracy over the entire range of H₂O concentrations of interest. This is true because of the relatively large amount of interference by H₂O and because the output of the H₂O monitor is not exactly directly proportional to the interference on the methane channel. The circuits can be adjusted to account exactly for the H₂O interference at one value of H₂O concentration, but there is a small remaining error (usually less than 0.2 ppm of methane) for other H₂O concentrations that must be accounted for analytically. Values of the required analytical corrections have been determined experimentally for several different H₂O concentrations.

OPTICAL

The H₂O concentration is determined by comparing the transmission of the sample at two wavelengths, one in the region of strong H₂O absorption near 1.9 μ m and one in a nearby region of weak absorption. The optical components employed by the H₂O system are shown in Figure 6 with the heated enclosure for the GFC assembly. Components mounted inside the enclosure are shown as they would be viewed with the top off for the top view, and the back wall off for the side view. Detectors DA and DB and their associated filters, FA and FB, are mounted on an aluminum block, which is mounted in the top section of the heated enclosure. The spinning GFC assembly, which is mounted on the motor shaft inside the heated enclosure, is also shown in the figure.

When the sample cell is set at 20 passes, mirror C3 forms an image of the source adjacent to mirror C2 and next to lens L5. Energy from the beam exits from the sample cell and is used in the H₂O detection system. Lens L5, with a focal length of 10.1 cm, forms an image of mirror C3 near lens L6. Flat mirrors H1 and H2 are tilted 45° from the vertical, and this mirror combination raises the beam of energy exiting from the sample cell by 5.7 cm and directs the beam into the top section of the heated enclosure. Lens L6, with a focal length of 3.8 cm, forms images of slit 1 on detectors DA and DB.

Detectors DA and DB have photoconductive PbS elements, 4mm x 4mm, that are mounted on a small aluminum block as shown in Figure 6. Filter FA acts as a dichroic beam-splitter, transmitting a narrow spectral interval in the region of strong H₂O absorption near 1.9 μ m. The wavelengths not transmitted by filter FA are reflected to filter FB, which transmits a narrow spectral interval of weak H₂O absorption. The gains of the preamplifiers are adjusted

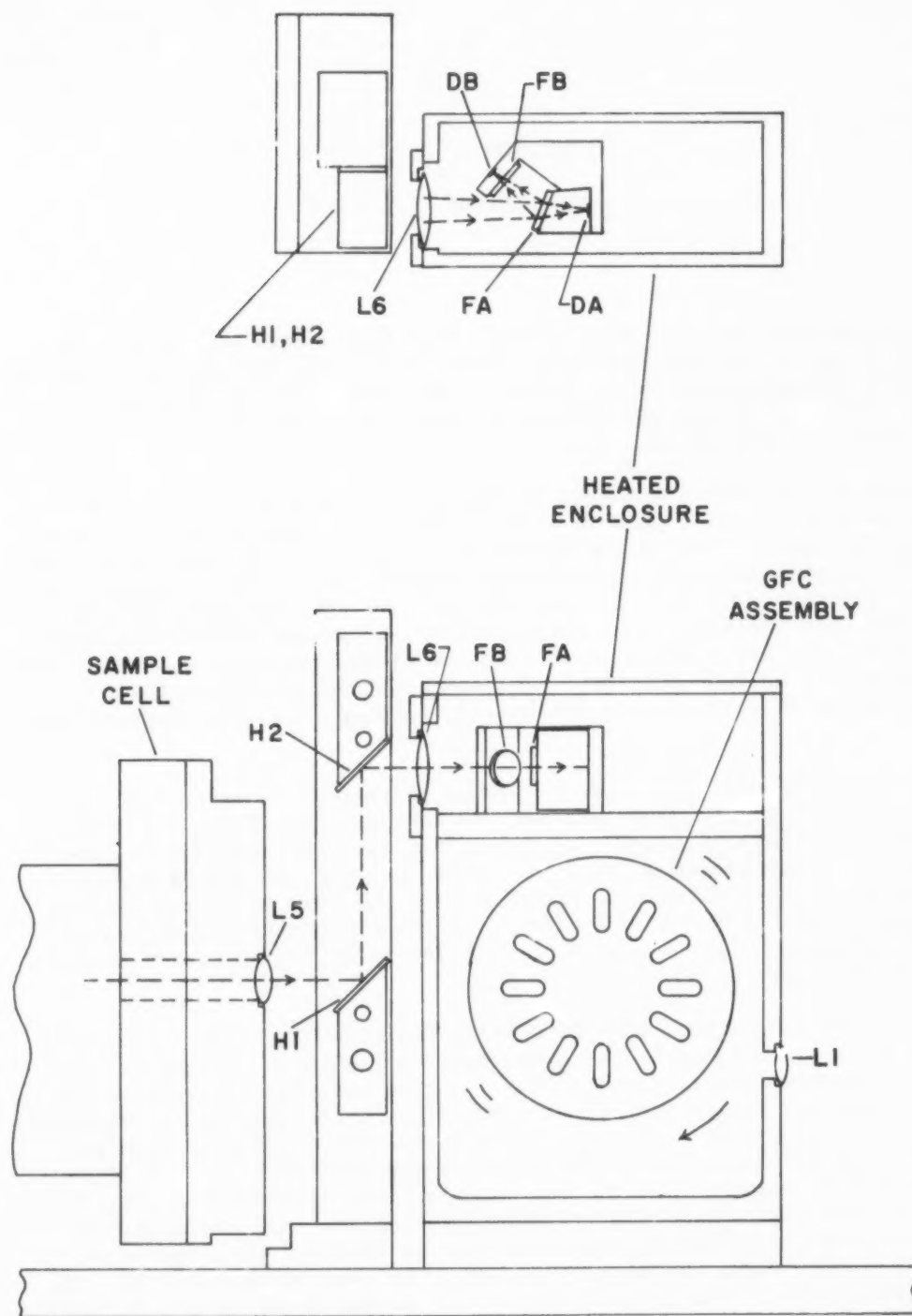


Figure 6. Optical diagram of the H₂O monitor.

so that the 360-Hz signals from the two detectors are equal when no absorbing gas is in the sample cell. It is apparent that the addition of H_2O to the sample cell reduces the amount of energy incident on detector DA more than it reduces the amount of energy incident on detector DB. The resulting difference in the detector signals is proportional to the H_2O concentration.

Since small variations in the temperatures of the detectors can produce drift in the zero-reading of the instrument, the temperature of the H_2O detectors and filters is maintained constant at approximately $50^\circ C$. A more stable and more accurate H_2O monitor employing only one detector could undoubtedly be designed. However, we have found from experience with similar instruments that this 2-detector type of monitor is adequate for the present purposes. By employing two fixed filters and two detectors, it has been possible to keep the optics relatively simple and not employ any moving optical components that are not otherwise required for the methane channel.

SIGNAL PROCESSING

The bias voltage for detectors DA and DB is provided by a ± 15 Vdc power supply used with the main electronics. A separate preamplifier amplifies the output of each detector, and the outputs of both preamplifiers are fed into a difference amplifier. When the sample cell is free of any H_2O , the monitor is zeroed by adjusting the outputs of the preamplifiers so that they are equal, thus producing a zero input to the difference amplifier. This is done with a fine zero control that is mounted on the front panel of the instrument and a coarse zero control that is mounted on the H_2O electronics card. The addition of H_2O to the sample cell creates a misbalance between the signals from the two preamplifiers and results in a signal from the difference amplifier. This signal passes through a tuned amplifier and is then demodulated to produce a dc voltage that is proportional to the H_2O concentration. A reference signal for the synchronous demodulator is obtained from the output of the preamplifier for detector DB.

A variable-gain amplifier makes it possible to adjust the "span" so that full-scale readings of the panel meter can be made to correspond to H_2O concentrations between approximately 1 percent and 10 percent. An output jack mounted on the instrument can be used to monitor the H_2O output signal. The H_2O output signal is also displayed on a panel meter mounted on the control panel.

An automatic gain control (AGC) circuit is employed so that the amplified difference signal is nearly independent of slight changes in such things as source brightness or dirt on windows that would change the amount of energy incident on both detectors by about the same factor. The AGC circuit maintains the signal from the preamplifier for detector B at a constant level. For example, if a change in the optics occurs that would ordinarily decrease the detector signal, the bias voltage is increased automatically to compensate for the decrease in radiant energy. The bias voltages for both detectors are increased by the same factor; therefore, to a good approximation, the change in bias voltage increases the outputs of both detectors by the same factor. It follows that a given output of the difference amplifier represents a certain

fractional difference in the outputs of the two preamplifiers. This difference can then be related to the H_2O concentration and is nearly independent of small changes in source brightness, dirt on windows, etc.

The H_2O correction circuits are adjusted so that the interference by approximately 1 percent H_2O is automatically accounted for exactly. For lower H_2O concentrations, there is a remaining interference error that has a maximum value corresponding to approximately + 0.1 ppm of methane when the H_2O concentration is 0.5 percent. For H_2O concentrations greater than 1 percent H_2O , the remaining interference error is negative and increases in magnitude with increasing H_2O concentration. At 3 percent H_2O , the remaining interference error that is not automatically accounted for corresponds to approximately - 0.2 ppm of methane.

SECTION 7

FLAME IONIZATION DETECTOR

The FID, a Beckman Model 400 Hydrocarbon Analyzer, continuously measures the concentration of hydrocarbons in a gas stream. The sensor is a burner in which a regulated flow of sample gas passes through a flame sustained by regulated flows of fuel gas (40 percent H_2 + 60 percent He) and air. The hydrocarbon components of the sample gas undergo a complex ionization in the flame and produce electrons and positive ions. Polarized electrodes in the sample chamber collect these ions, causing an electrical current that is proportional to the rate at which carbon atoms in hydrocarbons enter the burner. It follows that this current is directly proportional to the concentration of hydrocarbons if the flow-rate of the sample gas is maintained constant. The requirements for sensitivity and stability of the FID for the present application are more demanding than most applications of this model. Therefore, it has been necessary to make a few changes to the original instrument in order to improve the performance.

The stability of the zero-setting was improved by replacing the temperature controller with one of a different type that delivers power to the heater in proportion to the "error" temperature, the difference between the control temperature and the actual temperature of the sensor. A regular variation with a period of about 1 minute resulted in the zero-setting from the cycling of the original temperature controller.

Because of the sensitivity of the FID to any hydrocarbons in the sampling chamber, it is essential that the fuel and air that burn to form the flame is free of hydrocarbons. Bottled fuel and air of the highest quality available at reasonable prices may still contain hydrocarbon impurities at concentrations as high as a few hundred parts per billion. It is also very important that all the gas lines are free of any contaminants that contain hydrocarbons. We found that the best performance is obtained when activated charcoal filters are placed in the fuel line and air line to remove any remaining hydrocarbons from the gases before they enter the sampling chamber.

It is equally important that the zero-gas be free of hydrocarbons so that a reliable zero-setting can be obtained. Gas from the bottle of combustion air may also be used for zero-gas if it passes through the activated charcoal filter.

The sensitivity of the FID to a given number of carbon atoms in hydrocarbons depends somewhat on the particular hydrocarbon. Therefore, the most accurate measurements must take into account the particular hydrocarbon species that comprise most of the sample being studied. Fortunately, the sensitivity of the FID is nearly the same for most of the hydrocarbons that occur in relatively high concentrations in ambient air. Non-methane hydrocarbons (NMHC), the ones of primary interest, typically make up from 10 percent to 70 percent of the total hydrocarbons (THC). In order to determine the NMHC concentration accurately from the difference between the methane and THC readings, the

sensitivity of the FID to methane must be adjusted properly. The FID and methane monitor are calibrated simultaneously with a standard mixture of between 5 and 10 ppm of methane in air. Thus, the methane is accounted for properly. It is important that the methane sample used in the span calibration is free of other hydrocarbons; this can be ensured by passing the gas through an activated charcoal filter.

Drift in the zero-setting is probably the biggest source of error in measurements unless the precautions mentioned above are taken to ensure that the zero-gas and combustion gases are free of hydrocarbons. If hydrocarbons are adsorbed on the walls of the gas lines or the gas bottles, the concentration in the gas varies rapidly with changing temperature. Short-term noise (period less than 10 sec) corresponds to less than 5 parts per billion of methane.

The two most sensitive ranges of the FID are adjusted to give full-scale readings for 1 ppm and 10 ppm of methane. Sensitivities can be adjusted easily, and the output signal varies linearly with concentration of carbon atoms (in hydrocarbons) over concentrations normally occurring in ambient air.

SECTION 8

TESTS AND PERFORMANCE

The first part of this section summarizes a few of the tests performed on the entire instrument with the methane monitor and FID coupled together. Output signals were recorded separately for each monitor and are expressed in terms of ppm of methane. The sample cell of the methane monitor was operated at 2-atm pressure and 50°C.

The final two subsections deal with some experiments performed in an attempt to reduce the error in methane measurements due to the interference by H₂O in the sample gas.

PERFORMANCE OF METHANE MONITOR PLUS FID

SENSITIVITY AND NOISE

(Peak-to-peak noise level with 3 sec electronic time constant)

Methane Monitor: 0.05 ppm

FID: 0.005 ppm

LINEARITY

Methane Monitor: Linear for concentrations less than 10 ppm, only a slight deviation from linearity for concentrations between 10 and 20 ppm (see Figure 6).

FID: Not checked carefully, probably linear to beyond 20 ppm.

INTERFERENCES

Methane Monitor: (Without automatic correction) 2.5 percent H₂O produces interference corresponding to approximately +2.4 ppm.

(With automatic correction) No interference for 1 percent H₂O. Less than +0.1 ppm for lower H₂O concentrations; approximately 0.2 ppm at 3 percent H₂O.

FID: No significant interferences by normal atmospheric constituents.

TESTS ON PERMA-PURE DRYER

A Perma-Pure Dryer (Model PD-750) was tested as a means of reducing the H₂O in sample air to a sufficiently low concentration that it would not

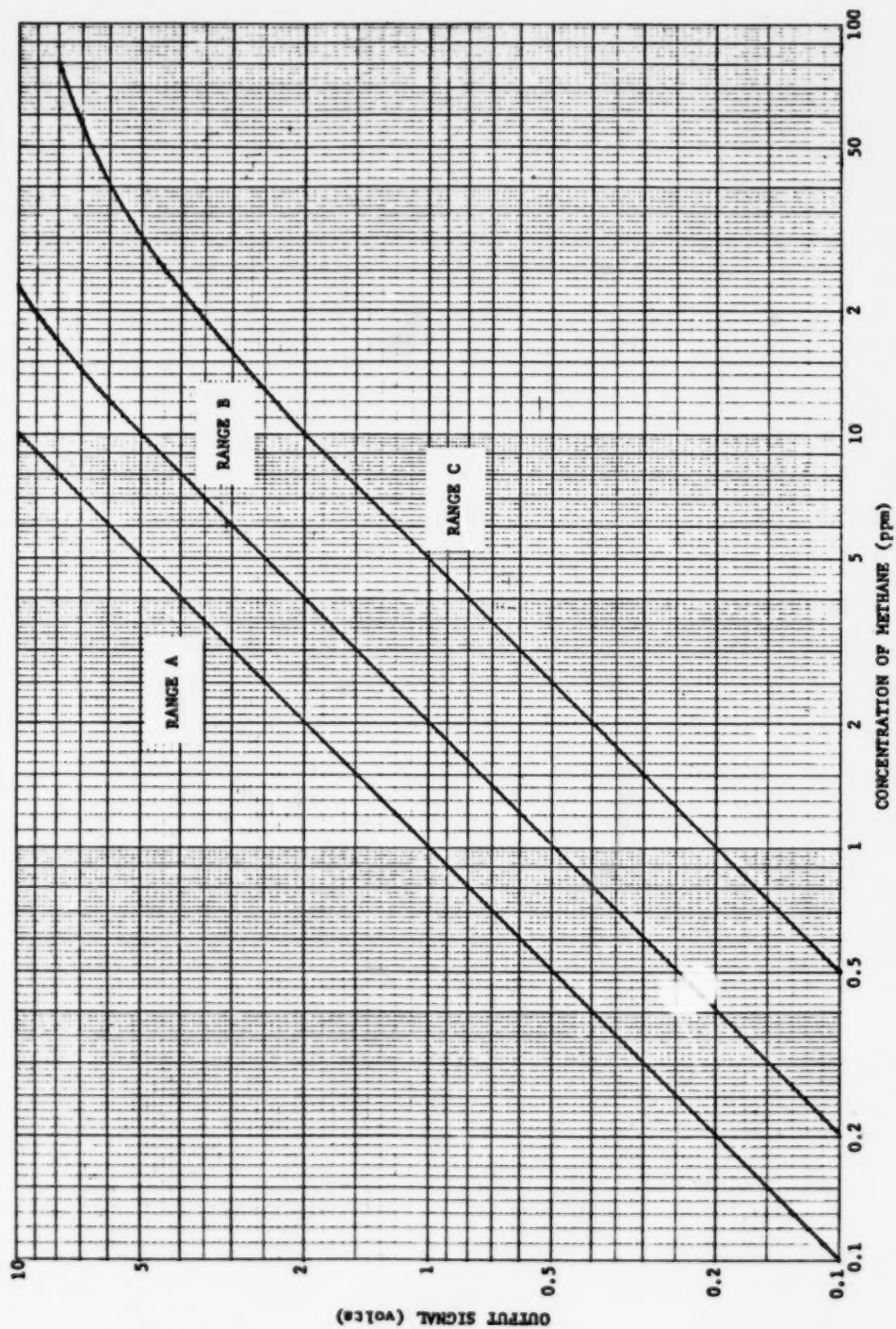


Figure 7. Approximate calibration curves for the methane monitor. The output signal is directly proportional to concentration for concentrations lower than shown.

interfere with the measurement of methane. Two important factors were tested: (1) the concentration of H_2O remaining in the sample gas after it had passed through the dryer, and (2) any possible change in the concentration of hydrocarbons in the sample gas. All of the tests were performed with the dryer at room temperature and in a manifold system that made it easy to direct gas through the dryer from a variety of sources. The samples included room air ethylene, hexane and methane. The dryer could easily be bypassed or switched into the gas stream while maintaining constant flow through the methane monitor or FID. Atmospheric pressure was maintained on the purge side of the dryer; either bottled N_2 or gas that had previously passed through the sample cell served as the purge gas. During most of the tests we monitored the output signals that represented total hydrocarbon concentration at the FID and H_2O and methane concentrations in the sample cell of the methane monitor. Different H_2O concentrations were obtained in the inlet gas by bubbling N_2 through water. Some of the tests were performed for several hours; during a long run the system was flushed periodically with zero-gas (bottled N_2 that has passed through a charcoal filter).

Our results indicate that the perma-pure dryer is capable of easily removing between 90 and 98 percent of the H_2O from normal air at flow-rates consistent with the requirement to maintain a short sample turn-over time. As an example, the sample cell of the methane monitor was maintained at 2-atm total pressure by pumping room air through the dryer into the sample cell, and a valve was adjusted to produce the desired flow rate while allowing the pressure to drop to approximately ambient air pressure before it passed through the purge side of the dryer. This method removed approximately 95 percent of the H_2O from room air. More H_2O can be removed if the inlet line and the sample cell are maintained at a higher pressure, such as 5-atm, with the purge side still at atmospheric pressure. The H_2O could probably be reduced to a negligible concentration by using a vacuum pump to reduce further the pressure of the purge gas.

Our tests indicate that the most serious drawback of the perma-pure dryer is that some hydrocarbons appear to adsorb on the walls of the dryer. In a typical test, we would pump room air through the system after it had been flushed thoroughly with N_2 for more than an hour. Several minutes were required for the hydrocarbon concentration measured by the FID to approach its equilibrium value. Similar results were obtained when a mixture of either hexane or ethylene was passed through the system instead of room air. A corresponding delay in the equilibrium condition was observed when the system was flushed with N_2 after it had contained room air or one of the mixtures of ethylene or hexane. The time required to approach equilibrium was much less if the same procedure was followed, except that the gas bypassed the perma-pure dryer. Our interpretation of the delay in equilibrium concentration is as follows: When the system has been flushed with N_2 for a few hours there is little or no gas other than N_2 adsorbed on the walls of the dryer. As room air starts flowing into the dryer, some of the hydrocarbon molecules adsorb on the wall of the tubing in the dryer. This process continues until the amount of adsorbed material is in equilibrium with the gas. The concentration of the hydrocarbon in the gas passing through the dryer is reduced until equilibrium is attained. The reverse process takes place when N_2 is flushed through

the system after it has contained a mixture of a hydrocarbon that is adsorbed. Thus, several minutes may be required to obtain an accurate zero-reading. The rate of adsorption or desorption is nearly independent of the flow rate or pressure of the purge gas. There is no evidence that any of the hydrocarbons pass through the wall of the dryer that separates the inlet gas from the purge gas.

The adsorption-desorption process is quite significant for room air or mixtures containing ethylene or hexane; however, it appears to be insignificant for methane. Essentially no delay, except for that required to remove the gas in the sample cell, was observed for the methane concentration to reach equilibrium when testing room air or a mixture of methane + N_2 . Water vapor also adsorbs on the walls of the dryer in much the same way that ethylene and hexane do. This does not create a serious problem because it is not important that the H_2O concentration in the ambient air be known accurately. The desorption of H_2O makes it necessary to flush with N_2 for several minutes to get an accurate zero-reading of the H_2O monitor.

The problem of adsorption of hydrocarbons can be overcome by rebuilding the gas-handling system so that the FID and the methane monitor are in parallel, rather than in series. In such an arrangement, the dryer is in the line to the methane monitor, but the gas to the FID does not pass through the dryer. The gas passing through the methane monitor is dried so that there is negligible interference by H_2O , and there is insignificant adsorption of the methane on the walls of the dryer.

Adsorption of a gas on the walls of a container usually decreases rapidly with increasing temperature. Therefore, it is quite possible that adsorption of certain hydrocarbons on the perma-pure dryer would decrease to a negligible level if the dryer were heated. This would make it possible to use the dryer in the line through which gas is directed to the FID. The dryer could be controlled at some temperature between approximately $50^\circ C$ and $100^\circ C$ without greatly complicating the gas-handling system.

It appears quite feasible to dry sample air with a perma-pure dryer to a sufficiently low H_2O concentration that the H_2O interference in the measurement is negligible. Additional tests with the dryer should be performed, particularly with the dryer at elevated temperatures. Other methods of accounting for H_2O interference should also be investigated so that the most convenient and reliable method can be determined.

REDUCING H_2O CORRELATION WITH GAS FILTERS

Concentrations of H_2O less than about 0.5 percent produce an interference in the output signal of the methane monitor that is approximately proportional to the H_2O concentration in the sample cell. However, as the H_2O concentration increases, the sensitivity to the H_2O decreases with the interference reaching a maximum corresponding to approximately 2.4 ppm of methane at 2.5 percent H_2O . As the concentration continues to increase further, the interference signal decreases. Because of the non-linear relationship between the H_2O concentration and the interference signal, the H_2O correction system described in

Section 6 is not capable of automatically accounting for the interference over the entire range of H_2O concentrations that may be encountered in ambient air.

The initial positive correlation that produces the positive interference at low concentrations of H_2O is apparently due to the near coincidence of three H_2O absorption lines with three strong methane absorption lines. Thus, the spectrum of H_2O is correlated positively with the spectrum of the methane in the gas-filter cell. At higher H_2O concentrations, these three H_2O lines become nearly opaque near their centers and most of the increase in H_2O absorption occurs at other wavelengths. The correlation between the spectra of the two gases becomes less positive, and for high concentrations it actually becomes negative. The three H_2O lines that cause the positive correlation at low concentrations occur too near the very strong methane lines in the Q-branch for it to be practical to employ a spectral bandpass filter that blocks the spectral region containing the H_2O lines.

Because of some of the disadvantages and potential problems of a system that removes H_2O from the air sample, it is desirable to sample the air without conditioning it before it enters the sample cell. With this in mind, we investigated a method of reducing the interference by H_2O in the measurement of the methane concentration. The approach involved using other gases that contain absorption lines near the H_2O lines that cause the interference. HCl , the first gas investigated, contains two lines centered near 3014.5 cm^{-1} and 3012.2 cm^{-1} .

All of these tests were performed with the versatile gas-filter correlation spectrometer built previously by Aeronutronic for EPA (D. E. Burch, F. J. Gates, D. A. Gryvnak and J. D. Pembroke, "Versatile Gas-Filter Correlation Spectrometer," Report EPA-600/2-75-024, August 1975). We made use of several features of this instrument that make it convenient for this type of test: (a) an adjustable grating monochromator can be adjusted to produce a spectral bandpass very similar to that of the methane monitor, (b) the gas-filter cell is stationary, rather than rotating, and can be changed or refilled easily, (c) another gas cell, called an attenuator cell, can be placed so that the monitoring beam passes through it during the half of each cycle when the beam is not passing through the methane filter cell, (d) still another gas cell, called a series cell, can be placed in series optically with the multiple-pass sample cell, and (e) an H_2O monitor measures the H_2O concentration in the sample cell.

Gas in the series cell blocks out energy at wavelengths corresponding to its strong absorption lines. This can reduce interference by a gas species in the sample cell if it has strong absorption lines at the same wavelengths as the lines of the gas in the series cell. Gas in the attenuator cell has the negative of the effect on the response that it would have if it were in the gas-filter cell. During the tests, we used several different combinations of HCl , ethane and ethylene in the series cell and attenuator cell. The gas-filter cell was filled with a mixture of methane plus nitrogen that was quite similar to the mixture used in the methane monitor. As part of a typical test, the output signal of the monitor was recorded as mixtures of varying concentrations

of H_2O in N_2 were flushed through the sample cell. This output signal was a measure of the interference produced by the H_2O .

The correlation between the spectral structures of H_2O and the other gases (HCl, ethylene, and ethane) caused the interference by H_2O to change when one of these gases was placed in the series cell or attenuator cell. As a typical example, 1-atm of pure HCl was placed in a 10 cm long series cell and the attenuator cell was evacuated. A neutral attenuator placed in the beam near the empty attenuator cell was adjusted to match the absorption by the methane in the gas-filter cell. The HCl in the series cell reduced the positive interference by low concentrations of H_2O by about a factor of 4. However, at higher H_2O concentrations, the interference became strongly negative. Other combinations of HCl in the series cell and attenuator cell changed H_2O interference in different ways, but no combination resulted in small interference over all H_2O concentrations up to 3 percent.

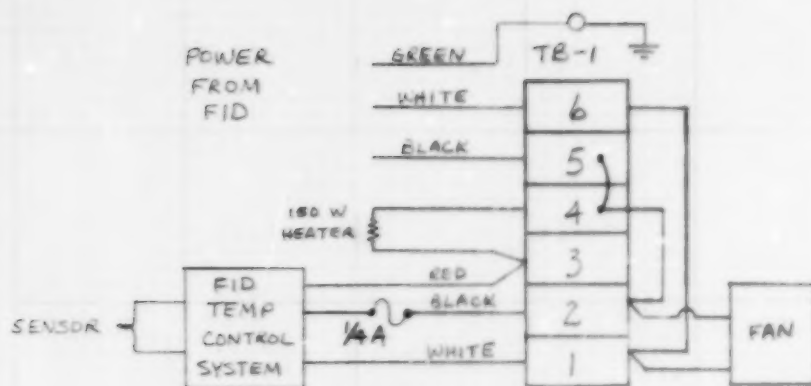
Different combinations of ethylene and ethane in the series cell and attenuator cell were also used. As with the HCl, the amount of interference by a given H_2O concentration could be reduced, but it was not possible to reduce the interference to a sufficiently low level for all concentrations of interest. If the positive interference at low H_2O concentrations was reduced significantly, the negative interference at high concentrations became worse.

As a result of these tests, we concluded that it is probably not feasible to reduce adequately the H_2O interference in the methane monitor by using spectral filters made from gases that have strong absorption lines near the H_2O lines that cause the strong positive interference. The H_2O interference can probably be accounted for more accurately by reducing the concentration of H_2O in the air sample before it reaches the methane sample cell. A device similar to the Perma-Pure Dryer described elsewhere in this section appears practical for this purpose.

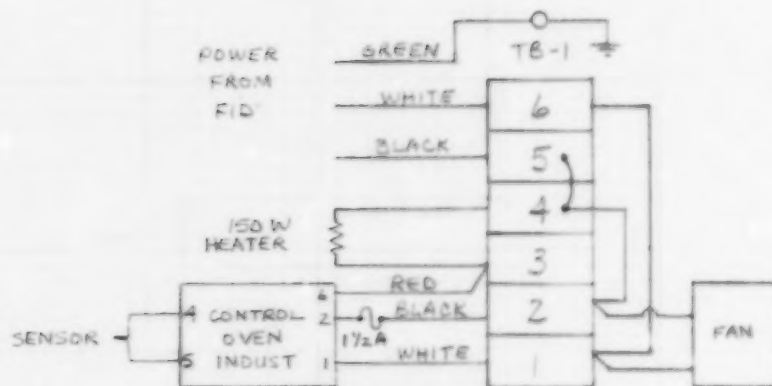
ELECTRICAL AND ELECTRONIC CIRCUITS

APPENDIX A

This appendix includes the electrical and electronic diagrams for the methane monitor and the pump assembly. Also included is a diagram of the minor changes made in the wiring of the FID. The Beckman Manual for the FID contains additional diagrams.



(A) ORIGINAL



(B) MODIFIED

Figure A1. The temperature controller for the FID was modified as indicated in the diagrams. The original FID controller supplied with the instrument caused the output signal to vary with a period of about 1 minute. The original controller was left in place, but it was disconnected electrically. An Oven Industries sensor controller was installed and adjusted to control the temperature at approximately 49°C. The original $\frac{1}{4}$ -amp SB fuse was replaced by a $1\frac{1}{2}$ -amp SB fuse. There is no evidence on the output signal of cycling when the Oven Industries controller is used.

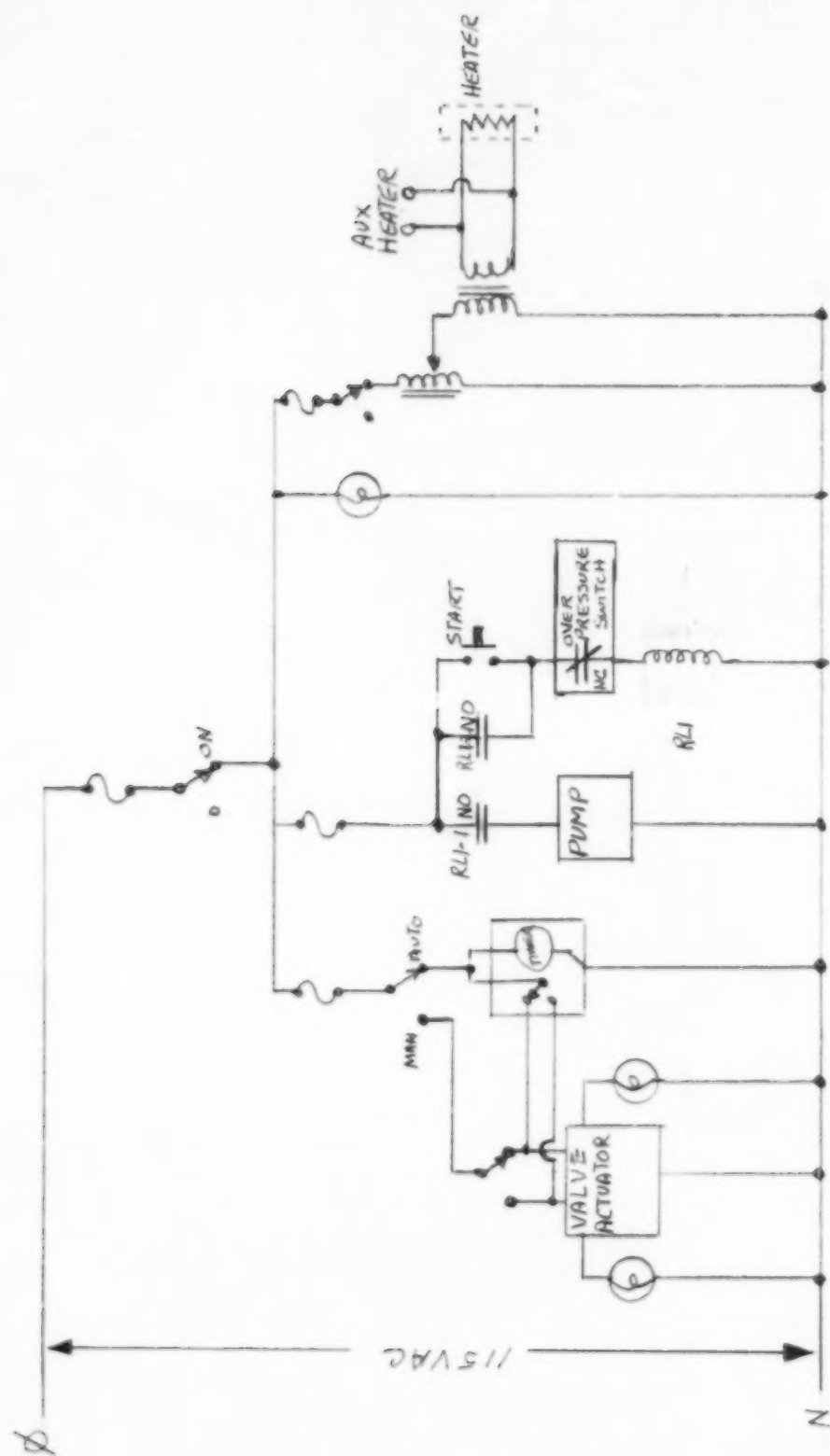


Figure A2. Schematic electrical diagram of the pump assembly.

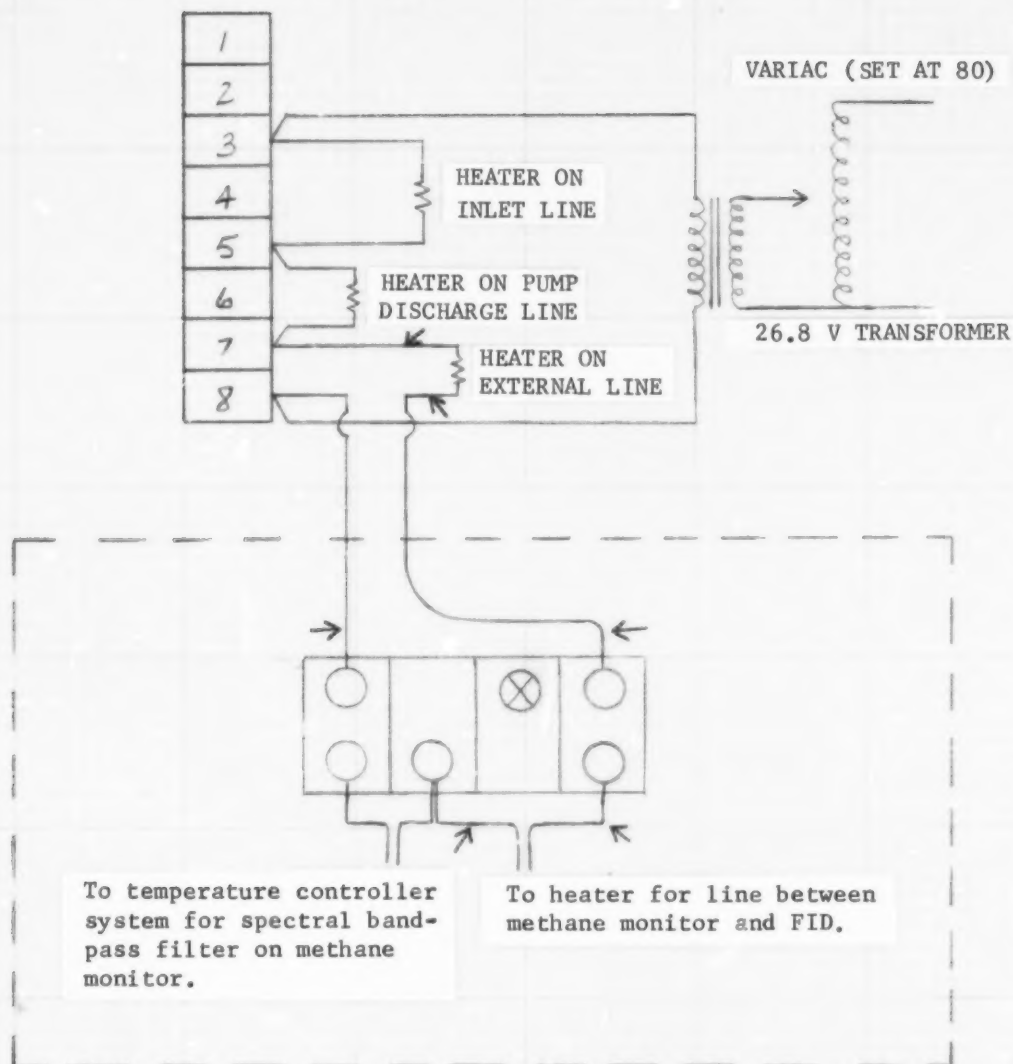


Figure A4. Wiring diagrams for heaters. Wires to be connected during set-up are indicated by arrows; others are wired permanently. The terminal strip enclosed in the broken lines is mounted on the methane monitor; the other terminal strip is on the pump assembly.

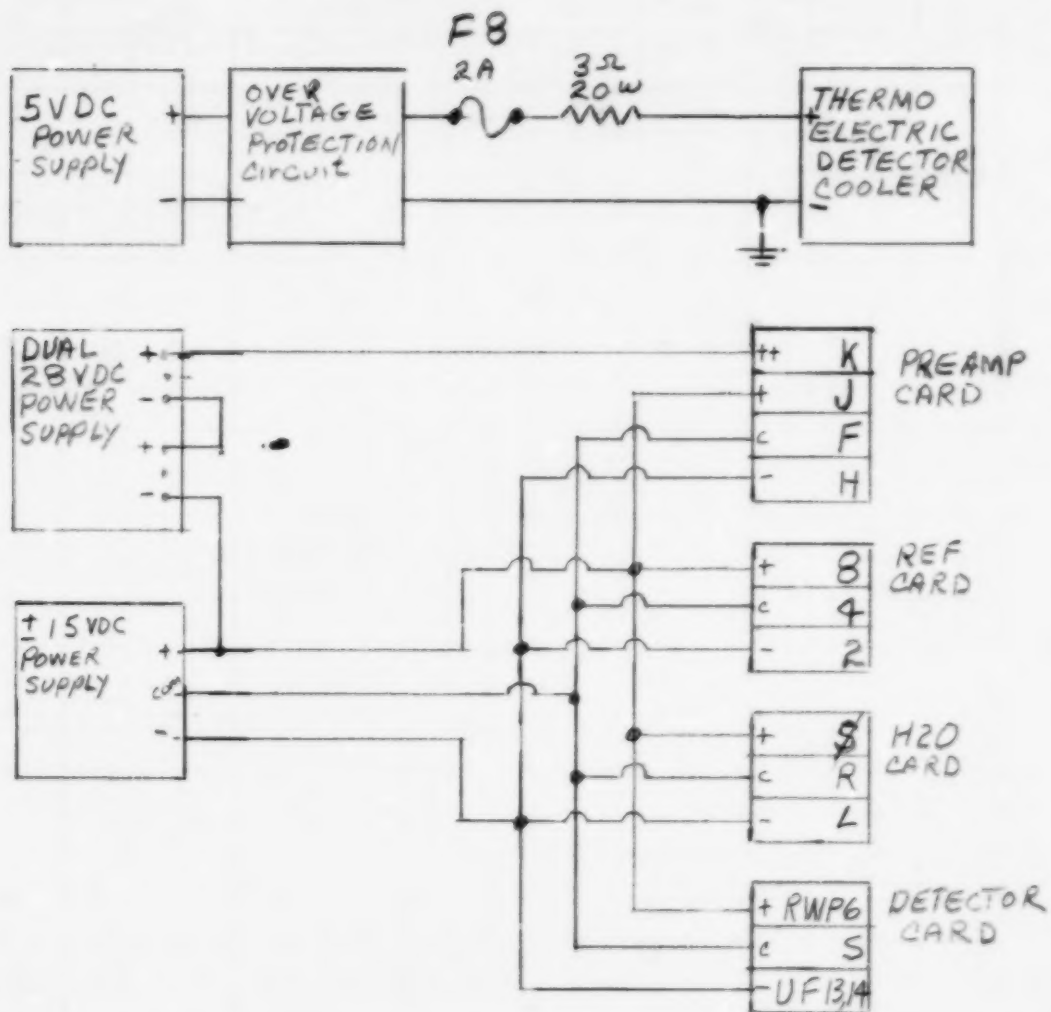


Figure A7. Schematic diagram for DC power distribution in the methane monitor.

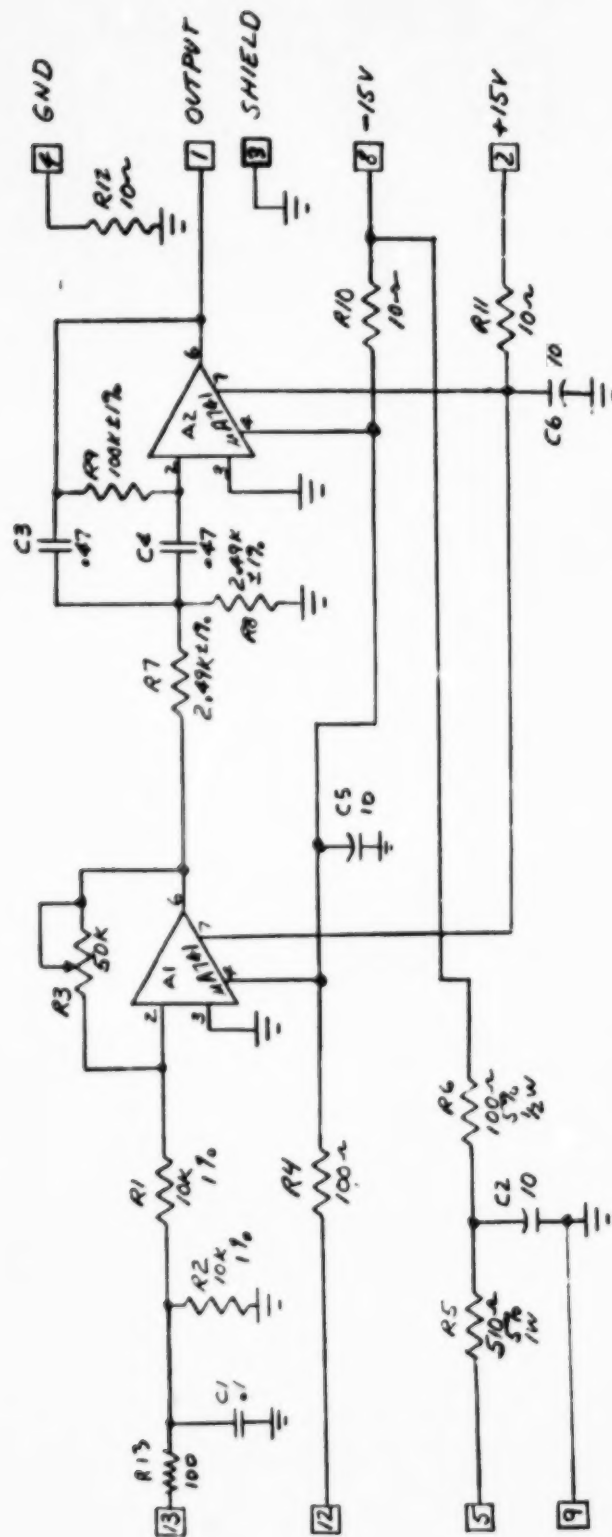


Figure A12. Schematic diagram of reference card.